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LIQUID PHASE EPITAXIAL GROWTH OF GALLIUM ARSENIDE

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S U M M A R Y

This report discusses two methods of liquid phase epitaxial (LPE) growth applied to the compound semiconductor gallium arsenide, and develops a mathematical description for each using a diffusion-limited model.

The properties of the epitaxial layers grown under various experimental conditions are discussed, and the observed growth rates compared with those predicted by the mathematical models. From the differences observed, it is concluded that processes additional to simple diffusion of solute through the melt are occurring. Convective mixing caused by horizontal temperature gradients within the melt is suggested as an explanation for these differences.

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1. INTRODUCTION

Epitaxial growth techniques provide excellent control over the purity and the crystalline perfection of many semiconducting materials. With GaAs for example the semiconductor injection laser is usually made from epitaxially grown material, because the very low defect density and the background impurity level required to achieve efficient radiative recombination are difficult to obtain by non-epitaxial methods. The phenomenon of epitaxial growth is of considerable scientific interest in its own right, but in addition the semiconductor lasers produced by epitaxy are small and efficient and of increasing importance in the fields of communications and surveillance. It is these considerations which have led to the work on epitaxial growth of GaAs to be described in this technical report.

Chemical vapour phase epitaxy and liquid phase epitaxy are both used extensively for the growth of semiconductors. However for the III-V compounds gas phase epitaxy tends to give poor compositional control in the grown layers because of difficulties in accurately controlling the gas phase compositions and because the group V elements dissolve in the group III source material. Thus for these compounds liquid phase epitaxy is preferred.

In this technical report we will examine some theoretical and practical aspects of two methods of liquid phase epitaxial growth, the temperature transient technique and the steady state differential technique. Because Laser Group possessed no facilities for epitaxial growth prior to 1976, the experiments described in this report were carried out at the Australian Post Office (now Telecom Australia) Research Laboratories in Melbourne from April to July 1974, and in the Electrical Engineering Department of Adelaide University from November 1974 to July 1975. At both centres the work was necessarily restricted by equipment which had been designed for other purposes. However, the experience gained during these periods, has allowed the design of a system for liquid phase epitaxy which has now been set up at DRCS.

2. METHODS FOR LIQUID PHASE EPITAXIAL GROWTH

Because the solubility of a dilute constituent such as arsenic in a liquid solvent such as gallium decreases with decreasing temperature, then if the temperature of an initially saturated solution is reduced, recrystallisation of gallium arsenide will take place. In the liquid phase epitaxial process, conditions are controlled so that the recrystallised material forms as a uniform monocrystalline deposit on a single-crystal substrate wafer.

In the temperature transient technique, (TTT), used at the Telecom Australia Research Laboratories, molten gallium doped with selected impurities is saturated with arsenic using an undoped gallium arsenide source, and then placed in contact with a gallium arsenide single crystal substrate. When this solution is cooled the melt becomes supersaturated, which causes precipitation of doped gallium arsenide and its subsequent nucleation in single crystal form on the gallium arsenide substrate. The rate of growth of the epitaxial layer depends upon the initial temperature and the rate of temperature decrease. Growth is terminated after the desired time interval by mechanically pushing the substrate out of contact with the melt. A slight variation of the technique used here allows the growth of multiple layers by pushing the substrate successively into contact with different melts, but for the work in this report only single layers were grown.

Because this type of epitaxial growth takes place at temperatures well below the melting point of the III-V compounds, high residual purity is generally obtained since the major impurities have low distribution coefficients at these temperatures. However, the effective impurity concentration changes with both temperature and growth rate, resulting in a spatially varying dopant concentration as the solution is cooled. For very thin layers this effect may be unimportant; however, for thick layers the variation in dopant concentration across the layer may be unacceptable.

In this situation it may be advantageous to use, as was done at Adelaide University, the steady state differential method (SSM) where growth takes place at a constant temperature. A temperature gradient established within the melt provides the driving force for diffusion of arsenic from the source gallium arsenide through the melt, to be deposited on the cooler substrate as an epitaxial layer of gallium arsenide. Although thick layers with uniform dopant concentration can be grown using SSM, the thickness of these layers cannot be as accurately controlled as in the TTT. This lack of precision is partly due to the greater number of variables which must be accurately controlled in the SSM, but in addition, the actual growth processes in the SSM are less well understood than in growth by TTT. This fact will become evident from the work discussed in this report.

In either method of LPE, slow growth rates encourage the homogenous incorporation of dopant impurities including those with distribution coefficients greatly different from unity. With sufficiently slow growth rates the melt composition is essentially constant right up to the growing film-melt interface, whereas, for high growth rates, growth may occur from a melt whose local composition can be very different from its average value. In addition the temperatures used for LPE growth are several hundred degrees below the melting point of the solid material being formed, so that diffusion from the substrate into the growing layer is minimised. This reduced temperature (compared to the usual bulk crystal growth methods such as Czochralski) decreases the level of contamination introduced into the melt from the growth system, and results in lower background impurity levels in the growing layer.

3. MATHEMATICAL FORMULATION OF LPE GROWTH

By making several simplifying assumptions about the growth processes, it is possible to derive mathematical models for the height of epitaxially grown layers. The validity of the assumptions can then be tested by comparing the predicted layer heights with those observed experimentally. The assumptions used in deriving the present model are listed below:

- (i) Transport of arsenic to the substrate takes place by diffusion through the melt from a source having uniform composition, to a sink (the growth surface) whose concentration at any time is determined by the temperature and therefore depends upon the particular growth technique employed.
- (ii) After the substrate is placed in the solution, the liquid melt and solid substrate are considered to be in equilibrium, with the concentration of arsenic at the growth interface determined from the liquidus properties appropriate to the temperature of the melt.
- (iii) Excess solute arsenic within several diffusion lengths of the growing interface is removed from solution only by epitaxial deposition on the substrate, and the presence of the substrate causes no edge effect perturbations.

- (iv) No recrystallisation of gallium arsenide occurs in the melt. This assumption is realistic since it is known that the dilute solutions used for LPE growth of gallium arsenide will withstand supercooling far in excess of that used for LPE, without spontaneous nucleation occurring.
- (v) There is no crystallisation of arsenic on the melt surface, and no loss of arsenic through evaporation into the hydrogen atmosphere which is the growth environment.
- (vi) The diffusion coefficient and the slope of the liquidus (solubility) curve may be considered constant over the small temperature interval of each growth run.
- (vii) Temperature uniformity exists within the solution in that there are no unplanned thermal gradients which could cause kinetic processes (such as convection) and perturb the uniformity of solution at the growth interface.

Very little fundamental data is available regarding this last assumption, but as will become evident later in this report, such factors may have a very great influence on the growth rates.

The temperature transient growth technique is the experimental method most frequently applied in overseas device technology, and some quite elaborate mathematical models have been developed (references 5 to 11). In the present work we have used a simplified approach based directly on the variation of arsenic solubility with temperature. Such an approach was suggested by Teede (reference 12), but his formulation has been somewhat modified by the present author. After developing a model for temperature transient growth, we will extend this approach to develop a model for the steady state temperature gradient technique. This latter model was derived from discussions with McRae (reference 13).

3.1 Temperature Transient Technique (TTT)

For simplicity in the following formulations, the chemical symbols Ga, As and GaAs will be used for gallium, arsenic and gallium arsenide respectively.

With the notation that

- $X_{As}(T)$ = solubility (atom fraction) of As in Ga at temperature T
- $n_{Ga}(\text{melt})$ = number of atoms of Ga solution added to the source from the melt
- $n_{GaAs}(\text{source})$ = number of atoms of GaAs dissolved from the source material
 $= n_{Ga}(\text{source}) + n_{As}(\text{source})$
- $m_{Ga}(\text{melt})$ = mass of Ga solution added
- $m_{GaAs}(T)$ = mass of source GaAs in solution at temperature T
- M_{Ga} = molecular weight of Ga (=69.72)
- M_{GaAs} = molecular weight of GaAs (=144.63)

then $X_{As}(T)$ = solubility (atom fraction) of As in Ga

$$= \frac{n_{As}(\text{source})}{n_{As}(\text{source}) + n_{Ga}(\text{source}) + n_{Ga}(\text{melt})}$$

Now $n_{As}(\text{source}) = n_{Ga}(\text{source}) = n_{GaAs}(\text{source})$

therefore

$$n_{GaAs}(\text{source}) = n_{Ga}(\text{melt}) \left[\frac{X_{As}(T)}{1-2X_{As}(T)} \right]$$

The mass of GaAs dissolved from the source material and in solution at temperature T_o is then

$$m_{GaAs}(T_o) = \frac{M_{GaAs}}{M_{Ga}} m_{Ga}(\text{melt}) \left[\frac{X_{As}(T_o)}{1-2X_{As}(T_o)} \right] \quad (1)$$

The amount of GaAs deposited from the source onto the substrate during a temperature reduction from T_o to T_1 , $m_{GaAs}(\text{Dep})$, is

$$m_{GaAs}(\text{Dep}) = m_{Ga}(\text{melt}) \cdot \frac{M_{GaAs}}{M_{Ga}} \cdot \left[\frac{X_{As}(T_o)}{1-2X_{As}(T_o)} - \frac{X_{As}(T_1)}{1-2X_{As}(T_1)} \right]$$

Using the abbreviation $X_{As}^1(T) = \frac{X_{As}(T)}{1-2X_{As}(T)}$, then

$$m_{GaAs}(\text{Dep}) = 2.074 m_{Ga}(\text{melt}) \left[X_{As}^1(T_o) - X_{As}^1(T_1) \right]$$

The density of GaAs is 5.32 g/cc, so that the height, h , of the epitaxial layer grown on a GaAs substrate of area A is

$$h = \frac{0.39}{A} m_{Ga}(\text{melt}) \left[X_{As}^1(T_o) - X_{As}^1(T_1) \right] \quad (2)$$

Layers grown at the Telecom Australia Research Laboratories using the TTT on substrate areas of approximately 0.6cm^2 and solvent masses $m_{Ga}(\text{melt})$ of approximately 1 gram, over temperature intervals $(T_o - T_1)$ of 50°C and 100°C and initial temperatures T_o of 700°C and 800°C , were observed to grow to approximately 60% of the magnitudes predicted by equation (2) when the liquidus data of Hall (reference 14) was used. This agreement is regarded as satisfactory in view of the greatly simplified approach taken in deriving equation 2. Several quite complex theoretical formulations for temperature transient growth have shown no better agreement with experimental observations.

3.2 Steady State Method

We will now consider a model suitable for use with the Steady State Differential Method, in which a temperature differential ΔT imposed across a solution causes a corresponding equilibrium solute concentration differential ΔC between source and substrate. In the absence of information on the fluid dynamics of the melt solution, we will formulate an equation under the assumption that solute diffusion is the process which limits the rate of growth of the epilayer.

In addition to the notation expressed in 3.1, we will use the following in this section

C = solute (source GaAs) concentration in the Ga melt, expressed in terms of the mass of dissolved GaAs per unit volume of Ga melt.

D = diffusion coefficient of As under a concentration gradient in the Ga melt.

$\frac{dT}{dx}$ = temperature gradient applied across the Ga melt.

$\frac{dC}{dx}$ = solute concentration gradient through the melt caused by the applied temperature gradient.

$\frac{dC}{dT}$ = variation in solute concentration with temperature.

ρ_{GaAs} = density of GaAs = 5.32 g/cc.

ρ_{Ga} = density of Ga = 5.95 g/cc.

From the law of diffusion we obtain the rate of mass deposition per unit area A to be

$$\frac{1}{A} \frac{d}{dt} \left(m_{GaAs}^{(Dep)} \right) = -D \cdot \frac{dC}{dx}$$

so that the rate of growth, $\frac{dh}{dt}$, of the deposited layer becomes

$$\begin{aligned} \frac{dh}{dt} &= \frac{-D}{\rho_{GaAs}} \frac{dC}{dx} \\ &= - \frac{D}{\rho_{GaAs}} \cdot \frac{dC}{dT} \cdot \frac{dT}{dx} \end{aligned}$$

Now from equation (1) in 3.1, we know that

$$m_{GaAs}(T) = \frac{M_{GaAs}}{M_{Ga}} \cdot m_{Ga}(melt) \cdot X_{As}^1(T)$$

Using this expression, and the definition of concentration in terms of dissolved mass per unit volume of melt, the concentration C of the solute near the source is then

$$C = \frac{M_{\text{GaAs}}}{M_{\text{Ga}}} \cdot \rho_{\text{Ga}} X_{\text{As}}^1 (T_{\text{source}})$$

and the concentration difference ΔC between source at temperature T_{source} and substrate at temperature T_{sub} is then

$$\begin{aligned} \Delta C &= \frac{M_{\text{GaAs}}}{M_{\text{Ga}}} \cdot \rho_{\text{Ga}} \left[X_{\text{As}}^1 (T_{\text{source}}) - X_{\text{As}}^1 (T_{\text{sub}}) \right] \\ &= \frac{M_{\text{GaAs}}}{M_{\text{Ga}}} \rho_{\text{Ga}} \cdot \Delta X_{\text{As}}^1 (T_{\text{source}} \rightarrow T_{\text{sub}}) \end{aligned} \quad (3)$$

Since the slope of the liquidus curve is constant over a small temperature interval ΔT , then

$$\frac{dC}{dT} = \frac{\Delta C}{\Delta T} = \rho_{\text{Ga}} \frac{M_{\text{GaAs}}}{M_{\text{Ga}}} \left(\frac{\Delta X_{\text{As}}^1 (T)}{\Delta T} \right)$$

If we can also assume that the temperature gradient within the solution, $\frac{\Delta T_s}{\Delta x}$, is constant over the distance between source and substrate, then

$$\frac{\Delta T_s}{\Delta x} = \frac{dT}{dx}$$

so that

$$\frac{dh}{dt} = D \frac{\rho_{\text{Ga}}}{\rho_{\text{GaAs}}} \frac{M_{\text{GaAs}}}{M_{\text{Ga}}} \left(\frac{\Delta T_s}{\Delta x} \right) \left(\frac{\Delta X_{\text{As}}^1 (T)}{\Delta T} \right)_{T_{\text{sub}}} \quad (4)$$

When the diffusion coefficient D is expressed in terms of cm^2/sec , and the solution temperature gradient $\frac{\Delta T_s}{\Delta x}$ in $^{\circ}\text{C}/\text{cm}$, then the expression for rate of growth of the epilayer $\frac{dh}{dt}$ becomes

$$\frac{dh}{dt} = 2.32 D \left(\frac{\Delta T_s}{\Delta x} \right) \left[\text{slope of curve } X_{\text{As}}^1 (T) - T \right]_{T_{\text{sub}}} \quad (\text{cm/sec}) \text{ or, of}$$

more practical use,

$$\frac{dh}{dt} = 8.35 \times 10^7 D \left(\frac{\Delta T_s}{\Delta x} \right) \left[\text{slope of curve } X_{\text{As}}^1 (T) - T \right]_{T_{\text{sub}}} \quad (\mu\text{m/hour})$$

Long et al (reference 15) have developed a more complicated diffusion equation:

$$\frac{dh}{dt} = \left(\frac{D}{\Delta x} \right) \log_e \left[\frac{\Delta C \text{ (substrate-solution interface)}}{\Delta C \text{ (source-solution interface)}} \right]$$

which under similar assumptions to equation (4) simplifies to

$$\frac{dh}{dt} = D \left(\frac{\Delta T_s}{\Delta x} \right) \frac{1}{T_{sub}^2} \left[\frac{\alpha \gamma}{\alpha - C_s \exp \left(-\beta + \frac{\gamma}{T_{sub}} \right)} \right] \quad (5)$$

where C_s is the concentration of As in solid GaAs and α, β, γ are constants. When the same values for D and $\left(\frac{\Delta T_s}{\Delta x} \right)$ are inserted in both equations (4) and (5), the calculated values for $\frac{dh}{dt}$ are substantially the same. Over the range of interest, the difference is about 5%.

To calculate values for $\frac{dh}{dt}$ with which to compare experimental observations we must first determine values for the diffusion coefficient D , the temperature gradient $\frac{\Delta T_s}{\Delta x}$, and the slope of the liquidus curve at each temperature of interest. Such values are discussed in Appendix 1, and the values shown in Table 1 are considered appropriate to the present situation.

TABLE 1.

T ($^{\circ}C$)	D (cm^2/sec)	Slope $\left[X_{As}^1 (T) - T \right]_{T_{sub}}$	$\frac{\Delta T_s}{\Delta x}$ $^{\circ}C/cm$
700	3×10^{-5}	0.90×10^{-4}	4.2
800	5×10^{-5}	2.78×10^{-4}	4.6

Using these values with equation(4), grown layer heights of 1.0μ /hour at $700^{\circ}C$ and 5.3μ /hour at $800^{\circ}C$ are predicted for the SSM. The rates observed, about 5μ /hour and 15μ /hour at $700^{\circ}C$ and $800^{\circ}C$ respectively, are much larger than the values predicted on the basis of diffusion limited growth. However, as reported in reference 16, convective forces caused by temperature non-uniformities in the furnace were found to have contributed to the epitaxial growth and greatly increased the deposition rate of GaAs from the saturated melt.

4. EXPERIMENTAL DETAILS

The various techniques for liquid phase epitaxial growth allow the formation of highly crystalline material with low defect and background impurity concentrations, together with the ability to introduce donor and acceptor impurities in a strictly controlled manner. To achieve these properties, the individual aspects of the growth process must be carefully considered and optimised. The major areas requiring detailed consideration are:

- (i) temperature control
- (ii) growth vessel
- (iii) growth environment
- (iv) substrate material preparation
- (v) source material preparation
- (vi) melt preparation
- (vii) impurity dopants
- (viii) loading procedure.

4.1 Temperature control

In both growth methods, stability and accurate control of the melt temperatures are imperative. The SSM used a split furnace whose upper element was maintained at a lower temperature than the bottom element, creating a temperature gradient across the furnace and thus across the melt solution. The temperature gradient and the actual temperature in the melt should be constant over at least the region where the melt contacts the substrate. The great importance of this requirement is demonstrated in later sections. The furnace used in the TTT had a uniform temperature throughout the operating volume, and this temperature was accurately controlled to produce a steady cooling rate in the furnace over a period of several hours. In the experiments reported here, furnace temperatures in the range of 600°C - 900°C were used, with applied temperature differentials of 0° , 50° or 100°C , and various cooling rates in the range of $15^{\circ}/\text{hour}$ to $50^{\circ}\text{C}/\text{hour}$. The various furnace temperatures were set using commercial controllers which were supplied with the respective furnaces, while the cooling rates in the TTT were controlled by an electronic ramp generator. Temperatures were monitored in all cases using chromel-alumel thermocouples, although it has since been realised that this was not the optimum choice.

4.2 Growth vessel

A cylindrical quartz tube within the furnace contained the growth vessel, whose background contamination had previously been reduced to a low level by vacuum baking at high temperatures followed by baking for an extended period in a flowing hydrogen atmosphere while loaded with gallium. For the TTT a machined pyrolytic graphite sliding boat with several wells or bins containing the respective melts was used for multiple layer growths. The substrate wafer was moved from bin to bin at certain times in the temperature cycle, and at the completion of growth was moved out of contact with any melt. The simpler boat which was used for the growth of the single layers reported here is illustrated schematically figure 1(a).

The vessel in use at Adelaide University for the SSM is illustrated in figure 1(b). This consisted of a vitreous carbon crucible in which the source block was held down by a graphite peg. The substrate, typically 5 mm x 10 mm, was held by suction onto a pyrolytic graphite holder. Movement of the substrate and holder was manually controlled from outside the furnace by a long quartz rod, and growth was initiated (or terminated) by rotating the substrate holder down into (or up out of) the melt solution.

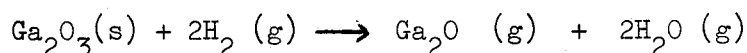
4.3 Growth environment

The crucible environment must be controlled during the growth process to avoid oxygen contamination.

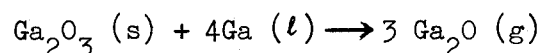
Any oxygen introduced during the loading operations or from small air leaks in the system influences the properties of the growing layer (references 17, 18, 19). Adsorbed oxygen on the surface of the carbon growth vessel or the walls of the quartz furnace tube is driven off at the temperatures used during the growth cycle and rapidly forms a layer of Ga_2O_3 on the melt surface (reference 20). Such a layer inhibits

'wetting' of the GaAs substrate by the liquid Ga melt, and causes areas of uneven growth upon the substrate. It is therefore advantageous for the growth to be carried out in a reducing atmosphere, such as hydrogen, which has been previously purified by passage through a heated palladium element and a liquid nitrogen trap.

At a melt temperature of the order of 800°C any surface trioxide, Ga_2O_3 (B.P. 2500°C), will react with hydrogen to form the suboxide, Ga_2O (B.P. 700°C), (reference 20) which will then be vaporised and removed by the hydrogen steam (which is flowing at a fixed rate within the range of 100-200 cc/minute)



However, a trioxide layer may also be formed between the gallium melt and the carbon walls of the growth vessel. At high temperatures the trioxide is converted to a gaseous suboxide by reacting with the gallium melt.



Complete removal of this Ga_2O then depends on the suboxide dissolving in the melt and vaporising at the melt-hydrogen surface. This will be a slow process because of its low solubility in the melt. Extended periods for equilibrium between the melt, the source material and the growth vessel are thus necessary before the substrate is brought into position and the growth cycle commenced. The long equilibrium time also minimises impurity levels, since impurities from the source are largely removed by extraction into the gallium melt and vaporisation into the hydrogen stream.

The volatile oxides and impurities driven from the melt could react with the substrate surface and cause an irregular masking effect. This would later result in uneven contact of the gallium melt on the substrate surface, and cause consequent non-uniform epilayer growth. It was found that more uniform junctions and better epilayers were formed if contact of the substrate with the volatile impurities was avoided, and this could be achieved in both growth systems by suitable positioning of the substrate for the long period before it was brought into the growth position.

4.4 Substrate material preparation

Cutting wafers from a bulk GaAs ingot with a diamond saw may produce work damage extending into the wafer at least $25\text{ }\mu\text{m}$ from each sawed surface (reference 21). Layers grown directly on such damaged surfaces exhibit gross surface and structural irregularities and so the damage was removed from the substrate by mechanical and chemical polishing before epitaxial growth was commenced.

For these experiments, each wafer was then cut into individual substrates $5\text{ mm} \times 10\text{ mm}$ using a wire saw. Three or four substrates were positioned equidistant around the perimeter of a flat circular glass plate $2\frac{1}{2}$ " diameter and $\frac{1}{4}$ " thick using resin wax (glycol phthalate) as adhesive.

The substrates on the plate were mechanically lapped using 3200 mesh carborundum suspended in glycerine, followed by careful washing in distilled water. This disc was then placed under a similar disc (a block $\frac{1}{2}$ " thick was found necessary to produce sufficient pressure, 30-60 g/cm², for flat and regular polishing), and chemical polishing undertaken by mechanical motion on a Pellon Microcloth. A 1:40 solution of "White King" commercial bleach in distilled water was used as the source of hypochlorite for the polishing liquid. Polishing action occurred through the formation on the substrate surface of gallium oxide, which was then removed by the Pellon pad. No abrasive was used in the chemical polishing technique, so that work damage was held to a minimum. For this reason, unless saw damage on the original wafer was very bad, it was preferable to omit the mechanical polishing stage and proceed directly to chemical polishing. Because dust particles produce fine scratches on the substrate surface, it was important for all polishing to be carried out in a clean environment. After polishing, the substrates were removed from the glass disc by heating the resin wax, and cleaned with acetone and alcohol before storage under methanol in individual containers.

Immediately prior to loading into the growth system, the substrate was ultrasonically cleaned sequentially in acetone and alcohol, etched in a 3:1:1 mixture of $H_2SO_4:H_2O_2:H_2O$ for 5-10 seconds to remove the thin surface oxide layer and thus expose a fresh clean surface of GaAs for the growth interface, then rinsed in distilled deionized water and ultrasonically cleaned in methanol or isopropyl alcohol. The figures quoted above for etchant composition and for the time of immersion were decided upon as optimum, as it was found that much longer in the etch solution produced marked surface deterioration.

4.5 Source material preparation

Long, (ref. 22), reported that GaAs layers grown from an undoped melt using single crystal GaAs source material had lower impurity concentrations than layers grown from a similar melt using polycrystalline source material. He attributed the difference in doping levels in the epilayer to excess impurities concentrated at the grain boundaries of the polycrystalline source, and recommended that polycrystalline GaAs should only be used if the grain boundaries could be cut away and discarded. In Melbourne, polycrystalline undoped material supplied by Monsanto was used as the source, cut to fit within a 5 mm x 10 mm region in the sliding boat. In Adelaide, undoped single crystal source material, boat grown by Bell and Howell was used. This was sawed into slices 2 mm to 3 mm thick and cut to a size sufficient to cover the entire bottom of the crucible. Each time a new melt was prepared, the source block was polished, cleaned and etched in a manner similar to that used for the substrate material, and loaded into the furnace as rapidly as possible. Each melt mixture contained a large excess of solute, and could thus be used for several successive growths. According to equation (1), a 30 gm melt is fully saturated by 0.42 gm of gallium arsenide at 700°C or by 1.5 gm at 800°C. The loss in weight of the solute block after single runs at these temperatures was, in fact, very close to these calculated values.

4.6 Melt (solvent) solution

As the solvent gallium was of very high purity when purchased, no further cleaning was attempted. The Ga was known to have a low copper content, which is important since copper will diffuse rapidly into epitaxial layers and can cause undesired intrinsic layers.

Initially, gallium of seven 9's purity from Alusuisse Metals was used, with 30 gm batches supplied in plastic bottles. To minimise contamination from the plastic, the bottles were refrigerated until immediately prior to use. When required, the bottles were warmed and the liquid contents (melting point 29.8°C) poured over the source material, the contents of a 30gm bottle covering the block to a depth of about 7 mm in the Adelaide SSM apparatus. Because so many different melts were being used for different doping experiments and temperature profiling, as well as for growth of undoped layers, gallium of six 9's purity supplied by Cerac was decanted from a 1000 gm bottle into batches of 30 gm then stored and used as detailed above.

In the TTT apparatus, sufficient liquid metal was squeezed from the plastic storage bottle to fill the small bin and the bottle was then resealed and refrigerated until the next use. On each occasion only a small amount of solvent was used, of the order of 1 gm per growth run.

4.7 Impurity dopants

The attempts to grow epilayers doped with a specific concentration of zinc and silicon which were carried out using the SSM were not very successful, but for completeness are reported below.

4.7.1 Zinc doping

This group II element acts as an acceptor and should form p doped layers. For zinc concentrations less than about $2 \times 10^{19} \text{ cm}^{-3}$, essentially all the zinc atoms are ionized at room temperature and so there is very little neutral (uncompensated) zinc. The liquidus isotherms of Jordan (reference 24) were used together with the ternary phase diagram Ga-As-Zn of Panish (reference 25) to calculate the mass of dopant Zn which should be added to a Ga melt in order to achieve specific dopant levels in the epitaxial layer. However, when zinc was added to the melt, a grey-black deposit formed on the quartz furnace tube at the operating temperature. This occurred for both powdered and solid zinc and presumably results from the high vapour pressure of zinc (about 250 torr at 800°C). The measured high resistivity of the epilayer suggested that little zinc had been incorporated into the growing layer, and, indeed, examination with DRCS X-ray equipment could detect no zinc at all.

Some interesting Ga-Zn-As compounds with definite crystallinity were formed as long silver-grey threads elsewhere in the cooler parts of the tube. The phase diagram suggests that this could be either Zn As_2 or the higher melting point Zn_3As_2 . However, the material has not yet been analysed.

4.7.2 Silicon doping

Since the group IV element Si is an amphoteric dopant whose behaviour is controlled essentially by the As vapour pressure, it can be used for either n or p doping. A GaAs crystal grown from a melt close to the stoichiometric composition, such as our seed crystal, becomes n type since Si is preferentially incorporated on Ga sites and acts as a donor. However, under reduced As pressure, as occurs at lower temperatures or in a Ga-rich melt, Si is predominantly incorporated as an acceptor on As sites and so a p type epilayer can be grown.

In the experiments conducted by many different research groups, a great spread has been observed for the temperatures at which the conductivity type changes from n to p for different silicon concentrations in the melt, and correspondingly large variations in the doping levels reported (references 26 - 31).

The ternary phase diagram Ga-As-Si proposed by Panish (reference 32) together with the liquidus data of Hicks and Green (reference 28) was used to predict the dopant concentration in the epilayer. In the experiments reported here, silicon of six 9's purity was used without any additional cleaning. When 0.85 atomic percent of silicon was added to a Ga melt saturated with GaAs, a smooth and shiny surface layer was grown at 800°C.

However, a "film" of whitish material appeared all over the melt surface and between the melt and the crucible wall. This film was present at the growth temperature, and did not appear only upon cooling to room temperature. Examination of the melt showed that less than 0.08 atomic percent Si had been dissolved. The solubility limit at 800°C (reference 33) should allow the dissolution of up to 5 atomic percent of silicon, so that all the added Si in the present case should have dissolved and been incorporated into the grown layer. A further attempt to dissolve Si in Ga was made after cleaning the Si for 15 seconds in a $\text{HF:HNO}_3 = 1.3$ "white etch". Again very little Si was dissolved and a similar white film was produced. Although the grown layer had a mirror-like surface finish, the junction was far from planar and a great deal of further experimentation undoubtedly needs to be carried out with the various dopants.

4.8 Loading procedure

After preparation and final cleaning, the source, substrate and melt were loaded under laminar flow conditions and placed in the furnace hot zone, ensuring minimum exposure to laboratory air during the loading operations by loading with a N_2 atmosphere flowing through the tube. The tube was evacuated and pure hydrogen admitted. Once H_2 was flowing through the tube at atmospheric pressure, the furnace elements were turned on and the melt and source allowed to equilibrate for 24 hours. Several runs were successfully carried out after only 14 hours equilibration, but whenever a fresh melt was used, patchy and uneven growths were obtained unless equilibration times of the order of 24 hours were allowed.

To initiate growth after the equilibration time, the substrate was placed in position in the melt, either by sliding in TTT, or rotating and dipping in the SSM crucible arrangement, and the desired temperature cycle begun. For best results, one further important step was carried out in the case of the TTT experiments. The melt temperature was raised by 1 to 2°C for a short time, to melt back the substrate surface about 1 μm and so remove any chemical impurities or mechanical damage remaining on the surface. This ensured a clean interface on which to grow the epilayer.

Upon conclusion of the growth cycle, the substrate was removed from the melt but not unloaded from the H_2 atmosphere until the furnace had cooled to room temperature. Frequently some unwanted Ga droplets adhered to the substrate surface and caused additional growth during the cooling period. The sliding boat technique used a scraper arrangement to minimise this adhesion and the consequent undesired growth, but the dipping technique relied only on gravity and surface tension to remove excess melt from the substrate surface.

5. PROPERTIES OF THE GROWN EPILAYERS

For acceptable yields using epitaxial growth in device technology, it is essential that the electrical and structural properties of the grown layers are well controlled and reproducible. The major properties of significance for device fabrication are surface morphology, layer thickness, junction planarity, doping level, and doping profile.

5.1 Surface Morphology

Despite great care in substrate preparation, macroscopic imperfections whose causes are not well understood, frequently occur in LPE layers. These imperfections can cause electrical inhomogeneities in injection lasers and Gunn oscillators and inhibit their operation. The most commonly reported surface morphologies on LPE GaAs are surface terraces, ripples, and cusps, whose shape and size may be dependent on substrate orientation. Bauser (ref 34) claims that substrates must be oriented to better than 5 minutes of arc to avoid terrace structure, whereas generally available substrate material is cut parallel to (100) planes only within 1° or 2° . The origin of these surface imperfections has also been attributed to substrate defects, dislocations, preparation residues and scratches, arsenic evaporation etc., interface attachment (substrate orientation, nuclei formations), and growth instabilities (constitutional supercooling, thermal fluctuations).

It had been believed that constitutional supercooling (the depression of the liquidus temperature of the melt at the melt-solid interface caused by depletion of the solute during growth) could result in an unstable growth interface and cause spurious nucleation of solid throughout the melt. Such nucleation in front of the substrate surface might result in metallic inclusions, non-uniform growth, and cellular growth structures in the epitaxial layer. However it is now known that there is considerable difficulty in nucleating the growth of GaAs from Ga-rich solutions. Saturated solutions can routinely be supercooled by greater than 5°C without any spontaneous nucleation occurring, and they can withstand appreciable supercooling even when in contact with a GaAs substrate. Thus if a solution which is just saturated (i.e. at its liquidus temperature) is placed in contact with a substrate at the same temperature (in exact equilibrium), the nucleation will tend to occur only on a relatively small number of favourable sites. Because of the high mobility of molecules in solution, these "islands" will tend to grow at the expense of later forming sites, and gradually form a structured surface. Solomon (ref 19) and Longo (ref 35) have claimed that the growth will remain discontinuous until a thickness greater than $1\text{ }\mu$ has formed. Supercooling the solution before inserting the substrate (not easily done with the steady state method) will increase the driving force for nucleation and overcome the surface barrier to growth which is evident at equilibrium, thus allowing the growth of smoother and more uniform layers. By using this technique, Bell Telephone Laboratories (USA) and Standard Telecommunications Laboratories (UK) have in fact grown planar layers as thin as $0.04\text{ }\mu$, in multiple layer growths (ref. 36, 37).

For the steady state growth method used in Adelaide, probably the overriding effect on surface quality and layer thickness is the incomplete drainage of the melt from the film surface after removal from the melt. Before it is lifted from the melt the substrate holder is rotated as far as the crucible size permits, but this is still substantially less than the 90° required for gravity and surface tension to achieve their maximum drainage effect.

The surfaces of these layers, with the exception of "tide-marks" sometimes noticed, are generally smooth and highly reflective to the naked eye, but exhibit pronounced surface structure when viewed under Nomarski interference contrast on an optical microscope. (Figures 2(a) and 2(b) for two separate substrates grown by SSM show how great the variation in surface morphology is over each individual substrate).

5.2 Doping level and doping profile

Once the thickness of the grown layer has been determined (using the techniques described in Section 5.4) the average free carrier concentration over that portion of the grown layer under examination can be determined by measurements of the Hall effect. Measurements of the junction capacitance can also be used to predict doping levels, and can in addition indicate whether the grown layer forms an abrupt junction or whether diffusion of carriers has taken place, which would result in a graded junction. Although these techniques were used at the Telecom Laboratories on some gallium arsenide samples having p-n junctions formed by diffusion, no such analyses for epitaxial samples were at that time attempted.

5.3 Junction Planarity

If the substrate was positioned directly above the melt during the equilibration period where it was exposed to volatile material driven off from the melt, the layers often grew unevenly. Patchy growths of this nature are seen in figures 3(a) and 3(b), where a series of mesas have been formed on the substrate. This type of behaviour was most pronounced whenever a new melt was used for the first time.

When the substrate was protected from the vapours until immediately prior to the commencement of growth, good flat junctions over most of the substrate were routinely achieved. The junctions were made visible by cleaving the substrate along (110) planes and staining the cleaved section with a solution of $1\text{HF}:3\text{HNO}_3:4\text{H}_2\text{O}$ for 15-40 seconds. Differences in electron densities in the differently doped regions affect the rate at which GaAs reacts with the staining solution, and the difference in etching rates causes the junction to become visible under a microscope. (This method requires different doping levels, but not necessarily different carrier types - although p-n junctions are better delineated than, for example, undoped -n or n-n⁺ junctions).

The typically flat junction formed on a substrate is shown in figure 4. However edge effects of some sort are present, as the junctions are frequently not flat near the edges of the substrate, and odd shaped overgrowths are also sometimes observed at the corners. The very irregular junction obtained after the attempted growth of a silicon doped epilayer (described in Section 4.7.2) is shown in figure 5.

5.4 Epilayer thickness

The thickness of a grown layer was measured after the cleaving and staining procedure mentioned in Section 5.3. To view the delineated junctions and estimate the thickness of the grown layers, a Zeiss KK08 reflected light microscope was used with a Nomarski differential interference contrast attachment and a magnification of 128X. Calibration of the eyepiece scale yielded a value of 6.8 μ per small division at this magnification, so that the layer height could be resolved to within a few microns at each position. Figure 6 is a schematic representation of the thickness determined in this manner for one sample where steady state epitaxial growth was undertaken over a period of 2 hours at nominally 800°C (the furnace top element was maintained at 770°C while the bottom was maintained at 820°C).

It is evident that there is a great variation in the height of the epilayer over this substrate, and similar variations were found in most samples grown at Adelaide using the steady state method. However, as is more fully reported by the present author in reference 16, the precise variations in height of the grown epilayers differ for each sample. Long (reference 15) in the only published work using the SSM, has reported that 2:1 variations in layer height across the surface of a single substrate are common, and his observations are consistent with the present results.

6. DISCUSSION

The variable epilayer thickness over a given substrate, and the non-reproducibility of results from sample to sample, strongly suggest that processes other than simple diffusion of gallium arsenide through the melt from source to substrate are taking place. The layers grown by the Steady State method are in general much thicker than predicted by the diffusion equation developed in Section 3, which suggests that the transfer of solute material to the growth interface is greater than for diffusion-limited "steady state" conditions. In addition, under Nomarski differential interference contrast on an optical microscope the grown layers exhibit flow marks and irregular wave-like patterns on their surfaces. The irregular surface morphology might be explicable in terms of unstable conditions created at the growth interface by fluid motion. Any point on the surface of the growing layer would then be subjected to a supersaturation which varies with time.

If fluid motion is occurring in the melt, then kinetic processes such as convection will be operative. Convective forces could result from horizontal temperature variations within the melt, which will develop if the furnace temperatures are not strictly uniform in the longitudinal direction. In fact, when the Marshall split furnace used for SSM was carefully profiled (reference 16), the temperature of the top element at a horizontal distance 2 cm from the mid-position was found to be 15°C greater than the set temperature of 770°C at the mid-position, while the bottom element was reasonably uniform over this region. These large horizontal variations in the temperature differential ΔT across the furnace elements occur in the region where the substrate is positioned during a growth run, and thus would be expected to produce a horizontal variation in temperature within the melt itself. Such variations were indeed observed when a differential thermocouple probe was positioned actually within the melt (reference 16).

Because the solubility of gallium arsenide in gallium is temperature dependant, then the existence of horizontal as well as vertical temperature gradients within the melt will cause variations in solute concentration in both horizontal and vertical planes. Cellular convection in the melt could be caused by direct thermal gradients, or else by the solutal gradients formed by these temperature variations. In Appendix II we develop a treatment in terms of the Raleigh criteria (references 15, 38) to determine the conditions for the onset of convection produced by either temperature gradients $\frac{\Delta T}{\Delta x}$ or concentration gradients $\frac{\Delta C}{\Delta x}$. The results in Tables II.1 and II.2 for

the experimental configuration used in the SSM show that the direct contribution of the temperature gradient to solution instability is much less than the contribution of the corresponding temperature-induced concentration gradient. Thus solute gradients rather than thermal gradients are the driving force which cause convection to develop within the melt.

The Raleigh criteria predict that solution heights less than a critical value are necessary to ensure that convection currents do not develop.

If we label the critical values Δx_T and Δx_S to represent temperature-induced and solute-induced effects respectively, then the experimental conditions at 800°C with $\left(\frac{\Delta T_s}{\Delta x}\right) = 4.6^\circ\text{C/cm}$

yield

$$\Delta x_T = 10.9 \text{ mm}$$

$$\Delta x_S = 1.3 \text{ mm}$$

In the majority of growths carried out using the SSM, a 30 g gallium melt was used. This quantity of gallium provides a solution depth of 7 mm, while the substrate is positioned at heights varying from 2 mm to 5 mm. Thus it is clear that convection will be produced in this configuration, resulting in the non-uniform grown layers which were in fact observed.

Since this convection provides a mechanism for non-uniform growth, it must be eliminated, or at least controlled, to obtain uniform thickness and smooth surfaces for the grown epitaxial layers. The calculations in Appendix II demonstrate that very small heights (~ 1 mm) are necessary to inhibit convection effects when the GaAs substrate is placed towards the top of the solution. However if the substrate is placed below the saturated melt, and the temperature gradient is reversed (so that the substrate is still at a lower temperature than the source, and the solution is everywhere warmer than the substrate) then the depletion of solute which occurs adjacent to the substrate will result in a stabilising density gradient (ref 11, 15). There will be little tendency for solute-induced convection to develop, and temperature-induced convection should not develop until $\Delta x > 10$ mm. Using the SSM with the substrate below the melt, the Cornell group (reference 15) report that uniform epitaxial layers with heights close to those predicted by the diffusion - limited conditions of equation (4) were observed.

However for the type of devices of interest to DRCS, the temperature transient technique using a sliding boat arrangement with small melt size and with the substrate positioned under the melt bins is more attractive than the steady state method using large melt volumes in a relatively large crucible. The sliding boat technique permits the growth of several consecutive epitaxial layers merely by sliding the substrate from under one bin to under another. The layers may be of different compositions depending on the composition of each melt, and the thickness of each layer is controlled by the time the substrate is in contact with the corresponding melt. Carry-over of solution from bin to bin may be minimised by suitable construction of the slider.

On the other hand, using the steady state method where the substrate is positioned towards the top of the melt solution causes convection effects in the melt and consequent non-uniformities to develop in the growing layer. When the substrate is mechanically moved from one crucible to another in the attempt to grow multiple layers, there is likely to be a greater carry-over of solution than in the sliding boat technique. More importantly, since the surface of the first epilayer is not flat, subsequent epitaxial layers will not form flat junctions and the non-uniform multiple layers will not be of use for making practical devices. Although more uniform epitaxial layers will be grown if the substrate is held below the saturated melt rather than some distance above the source material, such a configuration is difficult to achieve with the present apparatus. In addition there is then no suitable way of moving the substrate to another crucible, so that multiple layer growths are not possible.

7. CONCLUSION

Epitaxial growth of gallium arsenide from the liquid phase is discussed for both the temperature transient technique and the steady state method, and the properties of epitaxial layers grown under a variety of experimental conditions and in two different laboratories are presented. The observed heights of the grown layers are compared with mathematical models which were developed for both growth processes. Although reasonable agreement is found between calculated and observed layer heights for the temperature transient technique, a very large discrepancy is found when the present form of the Steady State method is employed. The grown layers are much thicker than would be expected if the growth was limited by diffusion of solute through the melt, in addition to being of non-uniform thickness. The non-uniformity suggests that convection effects might be present in the growth solution, a possibility which is discussed at some length. It is demonstrated that for the apparatus used here for the steady state method, the temperature non-uniformities which are produced within the growth solution are indeed sufficient to allow convective forces to develop. The relative advantages of the two growth methods are discussed, and it is concluded that the temperature transient technique using a multiple-bin sliding boat is more suitable for forming the type of devices of interest to DRCS. The experience gained using the different techniques, and the realization of the critical importance of temperature uniformity and stability, have led to the design of an improved system for liquid phase epitaxial growth at DRCS. The very satisfactory initial results which have been obtained with this new system encourage the belief that it can fulfil the requirements of an "ideal" epitaxial system and enable the growth of uniform and controllable layers suitable for the manufacture of practical electro-optic devices.

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REFERENCES

- | No. | Author | Title |
|-----|--|---|
| 1 | Pilkuhn, M.H. | "The Injection Laser"
Phys. Stat. Sol. Vol. 25, p9-62
(1968) |
| 2 | Hall, R.N., Fenner, G.E.
Kingsley, J.D., Soltys, T.J.,
and Carlson, R.O. | "Coherent Light Emission from
GaAs Junctions"
Phys. Rev. Letters Vol.9,
p366-368 (Nov 1962) |
| 3 | Nathan, M.I., Dumke, W.P.,
Burns, G.E., Dill, F.H. and
Lasher, G.J. | "Stimulated Emission of Radiation
from GaAs p-n Junctions"
Appl. Phys. Letters Vol.1,
p62-65 (Nov 1962) |
| 4 | Quist, T.J., Rediker, R.H.,
Keyes, R.J., Krag, W.E.,
Lax, B., McWhorter, A.L.,
and Zeiger, H.J. | "Semiconductor Maser of GaAs"
Appl. Phys. Letters, Vol.1,
p91-92 (Dec. 1962) |
| 5 | Hsieh, J.J. | "Thickness and Surface
Morphology of GaAs LPE Layers
Grown by Supercooling, Step-
cooling, Equilibrium-Cooling and
Two-phase Solution Techniques"
J. Crystal Growth Vol.27, p49-61
(Dec 1974) |
| 6 | Rode, D.L. | "Isothermal Diffusion Theory of
LPE: GaAs, GaP, Bubble Garnet"
J. Crystal Growth Vol.20, p13-23
(Aug 1973) |
| 7 | Moon, R.L. and
Kinoshita, J. | "Comparison of Theory and
Experiment for LPE Layer Thickness
of GaAs and GaAs Alloys"
J. Crystal Growth Vol.21, p149-154
(Jan 1974) |
| 8 | Moon, R.L. | "The Influence of Growth Solution
Thickness on the LPE Layer
Thickness and Constitutional
Supercooling Requirement for
Diffusion Limited Growth"
J. Crystal Growth Vol.27, p62-69
(Dec 1974) |
| 9 | Crossley, I., and
Small, M.B. | "Computer Simulations of Liquid
Phase Epitaxy of GaAs in Ga
Solution" J. Crystal Growth
Vol.11 p 157-165 (Nov 1971) |
| 10 | Tiller, W.A., and
Kang, C. | "On the Growth Rate of Crystals
from Solution"
J. Crystal Growth Vol.2 p 345-355
(Dec 1968) No.6 |

No.	Author	Title
11	Small, M.B., and Crossley, I.	"The Physical Processes Occuring during Liquid Phase Epitaxial Growth" J. Crystal Growth Vol.27, p35-48 (Dec 1974)
12	Teede, N.	Private communication (Telecom Australia)
13	McRae, C.	Private communication (Adelaide University) and Ph.D. Thesis Adelaide University (1976) "Thermally Induced Frequency Instabilities in Transferred Electron Microwave Oscillators".
14	Hall, R.N.	"Solubility of III-V Compound Semiconductors in Column 111 Liquids" J. Electrochem. Soc. Vol.110, p385-388 (May 1963)
15	Long, S.I., Ballantyne, J.M. and Eastman, L.F.	"Steady State LPE Growth of GaAs" J. Crystal Growth Vol.26, p13-20 (Nov 1974)
16	Folkard, M.A.	"Measurement of Temperature Instabilities and their effect on the Liquid Phase Epitaxial Growth of Gallium Arsenide" ERL-0077-TR
17	Vilms, J and Garrett, J.P.	"The Growth and Properties of LPE GaAs" Solid State Electronics Vol 15 No. 4 p443-445 (April 1972)
18	Otsubo, M., Segawa, K., and Miki, H.	"The Influence of Oxygen on the Properties of GaAs Grown by Liquid Phase Epitaxy" Jap. J. of Applied Physics Vol 12, No 6 p 797-803 (June 1973)
19	Solomon, R.	"Factors Influencing the Electrical and Physical Properties of High Quality Solution Grown GaAs" Proc. 2nd Int. Conf. on Gallium Arsenide and Related Compounds (Inst Phys London 1969) Paper 3, p11-17.
20	Dawson, L.R.	"Growth of Thin Epitaxial GaAs Films from Ga Solutions" Thesis: University of Southern California (Jan 1969)
21	Tietjen, J.J., Abrahams, M.S., Dreeben, A.B., and Gossenberger, H.F.	"The Origin of Macroscopic Surface Imperfections in Vapour-Grown GaAs" Proc. 2nd Int. Conf. on Gallium Arsenide and Related Compounds. Dallas 1968 (Inst. Phys. London 1969) paper 9, pp55-58

No.	Author	Title
22	Long, S.I.	"Solution Growth of Gallium Arsenide" Rome Air Development Centre Technical Report RADC-TR-69-42 (March 1969)
23	Jordan, A.S.	"The Solid Solubility Isotherms of Zn in GaP and GaAs" J. Electrochem. Soc. Vol. 118, No.5, p 781-787 (May 1971)
24	Chang, L.L. and Pearson, G.I.	"The Solubility and Distribution Coefficients of Zn in GaAs and GaP" J. Phys. Chem. Solids Vol.25, p23-30 (Jan 1964)
25	Panish, M.B.	"The Gallium-Arsenic-Zinc System" J. Phys. Chem Solids Vol.27, p291-298 (Feb 1966)
26	Ahn, B.H., Shurtz, R.R., and Trussell, C.W.	"Dependence of Growth Properties of Silicon-Doped GaAs Epitaxial Layers Upon Orientation" J. Appl. Phys. Vol.42, No.11, p4512-4513 (Oct 1971)
27	Terramoto, I.	"Calculation of Distribution Equilibrium of Amphoteric Silicon in Gallium Arsenide" J. Phys. Chem. Solids Vol.33, No.11 p 2089-2099 (Nov 1972)
28	Hicks, H.G.B., and Green, P.D.	"Control of Silicon Contamination in Solution Growth of Gallium Arsenide in Silica" 1970 International Symposium on GaAs Paper 10, p92-99
29	Spitzer, W.G. and Panish, M.	"Silicon-Doped Gallium Arsenide Grown from Gallium Solution : Silicon Site Distribution" J. Appl. Phys. Vol.40, No.10, p4200-4205 (Sept 1969)
30	Panish, M.B. and Sumski, S.	"Ga-As-Si : Phase Studies and Electrical Properties of Solution- Grown Si-Doped GaAs" J. Appl. Phys. Vol.41, No.7, p3195-3196 (June 1970)
31	Moriizumy, T. and Takahashi, K.	"Si-and Ge-Doped GaAs p-n Junctions" Jap. J. Appl. Phys. Vol.8, No.3, p 348-357 (March 1969)
32	Panish, M.B.	"The Ga-As-Si Ternary Phase System" J. Electrochem. Soc. Vol.113, p1226-1228 (Nov 1966)
33	Keck, P.H. and Broder, J.	"The Solubility of Silicon and Germanium in Gallium and Indium" Phys.Rev.Vol.90 p521-522 (May 1953)

No.	Author	Title
34	Bauser, E., Frik, M. Loechner, K.S., Schmidt, L. and Ulrich, R.	"Substrate Orientation and Surface Morphology of GaAs Liquid Phase Epitaxial Layers" J. Crystal Growth Vol.27, p148-153 (Dec 1974)
35	Longo, J.T., Harris, J.S. Gertner, E.R., and Chu, J.C.	"Improved Surface Quality of Solution Grown GaAs and $Pb_{1-x}Sn_xTe$ Epitaxial Layers : A New Technique" J. Crystal Growth Vol. 15, No.2, p107-116 (July 1972)
36	Panish, M.B., Casey, H.C. Sumski, S., and Foy, P.W.	"Reduction of Threshold Current Density in $GaAs-Al_xGa_{1-x}As$ by Separate Optical and Carrier Confinement" Appl. Phys. Letters Vol 22, No.11 p590-591 (June 1973)
37	Thompson, G.H.B., and Kirkby, P.A.	"Low Threshold-Current Density in 5-Layer-Heterostructure (GaAl) As/GaAs Localised-Gain-Region Injection Lasers" Electronics Letters, Vol.9, No.13 p295-296 (June 1973)
38	Raleigh, Lord	"Scientific Papers", Vol.6 p 432 (1916) (Cambridge Univ. Press, Cambridge)
39	Dawson, L.R.	"Near Equilibrium LPE Growth of GaAs- $Ga_{1-x}Al_xAs$ Double Heterostructures" J. Crystal Growth Vol.27, p86-96 (Dec 1974)
40	Mlavsky, A.I. and Weinstein, M.	"Crystal Growth of GaAs from Ga by a Travelling Solvent Method" J. Appl. Phys. Vol.34, No.9, p2885-2892 (Sept 1963)
41	Tiller, W.A.	"Theoretical Analysis of Requirements for Crystal Growth from Solution" J. Crystal Growth Vol.2, No.2, p69-79 (April 1968)
42	Richman, D.	"Dissociation Pressures, GaAs, GaP, InP, Nature of III-V Melts" J. Phys. Chem. Solids, Vol.24, No.9 p1131-1139 (Sept 1963)
43	Thurmond, C.D.	"Phase Equilibrium in the GaAs and the GaP Systems" J. Phys. Chem. Solids Vol.26, No.4 p 785-802 (April 1965)
44	Swallin, R.A.	"Thermodynamics of Solids" Second edition Chapter 6 (Wiley, New York 1972)

APPENDIX I

I.1 Slope of the Liquidus Curve

The slope of the liquidus curve is obtained from Hall's solubility data (reference 14) which receives independent verification from Hsieh (reference 5) in a limited temperature range near 800°C.

TABLE I.1

T(°C)	X _{As} (T) (mole fraction/°C)	X _{As} ¹ (T) (mole fraction/°C)	$\frac{dX_{As}^1}{dT}$ (T) (mole fraction per °C ²)
700	6.50 x 10 ⁻³	6.59 x 10 ⁻³	0.90 x 10 ⁻⁴
800	2.32 x 10 ⁻²	2.43 x 10 ⁻²	2.78 x 10 ⁻⁴
900	5.69 x 10 ⁻²	6.75 x 10 ⁻²	7.98 x 10 ⁻⁴

I.2 The Diffusion Coefficient D

Diffusion coefficients for most liquids lie in the range 10⁻⁴ to 10⁻⁵ cm²/sec, with some temperature dependence observed. No direct experimental measurements of the diffusion of As or GaAs in a Ga solvent have been published. Instead, estimates for D have been made by comparing experimental growth rates with the predictions of various mathematical theories (references 5,6,7,39,40), and obtaining "best fit" values for D. There is a large variation in the values so obtained, but based on the published results, we consider the values of Table I.2 appropriate to the present experimental conditions.

TABLE I.2

T (°C)	D (cm ² /sec)
700	3 x 10 ⁻⁵
800	5 x 10 ⁻⁵
900	10 x 10 ⁻⁵

I.3 Solution Temperature Gradient $\left(\frac{\Delta T_s}{\Delta x}\right)$

Temperature probing within the melt was undertaken and is described in detail in reference 16.

To make these measurements, a thermocouple made from 0.025" diameter chromel and alumel wires was encased in thin quartz and positioned with its "hot" junction at the bottom of a probe which had dimensions similar to the substrate holder used in SSM growths. The probe was dipped into the melt and then raised or lowered a certain distance Δx as determined by a simple screw arrangement external to the tube. This was very crude, but allowed an order-of-magnitude determination of the temperature gradient. The repeatability of measurements from day to day, or even in successive cycles of the probe, was poor. However, the results indicated that the solution temperature gradient was almost independent of the actual furnace temperature and largely determined by the temperature differential between the top and bottom elements. For an element-to-element differential $\Delta T = 50^\circ\text{C}$, the solution temperature gradient was found to be of the order of

4.2°C/cm at 700°C and
4.6°C/cm at 800°C.

APPENDIX II

Convection Effects in Fluids

In a two component system, such as a gallium melt containing dissolved arsenic, there are two major processes which could contribute to natural convection. Instabilities may be created by either thermal gradients or concentration gradients in the solution. These potential instabilities are opposed by the viscosity of the fluid, which provides a damping force. However instability and consequent cellular convection will occur whenever a critical temperature gradient or a critical solute gradient (which may be temperature induced) is exceeded. These critical values depend on the particular experimental situation and geometry.

Raleigh (ref 38) originally showed that a fluid subjected to a purely vertical temperature difference ΔT across a depth of fluid Δx can be characterised by a Raleigh number R_T , where

$$R_T = g \Delta T \gamma \frac{(\Delta x)^3}{K \eta} = \frac{g \gamma}{K \eta} (\Delta x)^4 \left(\frac{\Delta T}{\Delta x} \right) \quad (II.1)$$

and γ = coefficient of volumetric expansion ($= 9.7 \times 10^{-5}/^{\circ}\text{C}$ at 900°C for Ga)

K = thermal diffusivity ($= 0.3 \text{ cm}^2/\text{s}$)

η = kinematic viscosity ($= 1.2 \times 10^{-3}$ Stokes at 800°C)

$g = 980 \text{ cm}^2/\text{s}$

(The values of the parameters quoted above were obtained from reference 15). Instability with respect to the thermal gradient occurs when the Raleigh number R_T exceeds a certain critical value R_c . For a fluid bounded by two solid surfaces, this critical value is $R_c = (1700 \pm 140)$. Thus instability will set in when

$$R_T > (1700 \pm 140).$$

If the solute is less dense than the solvent, it is possible to get density inversion within the melt when the substrate is at a lower temperature than the source and is located above the source (ref 11). An expression similar to equation (II.1) may be derived (ref 11, 15, 41) for differences in solute concentration ΔC over a distance Δx in the fluid.

$$\begin{aligned} R_s &= g \Delta C \beta \frac{(\Delta x)^3}{D \eta} = \frac{g \beta}{D \eta} (\Delta x)^4 \left(\frac{\Delta C}{\Delta x} \right) \\ &= \frac{g \beta}{D \eta} (\Delta x)^4 \left(\frac{\Delta C}{\Delta T} \right) \left(\frac{\Delta T}{\Delta x} \right) \end{aligned}$$

where β = volumetric change for unit concentration change

D = mass diffusivity ($= 5 \times 10^{-5} \text{ cm}^2/\text{s}$ at 800°C).

Instability with respect to the density gradient produced by a single solute sets in when

$$R_s > 1770.$$

When temperature gradients and solute gradients are both acting, as in the present experimental situation, then the individual effects will be superimposed. Because the thermal diffusivity K is much greater than the mass diffusivity D , the critical Raleigh number will be exceeded more readily as a result of concentration variations than as a result of temperature differences. When the critical value is exceeded by even a small value, steady convection cells are set up. If the critical value is exceeded by an order of magnitude or more, then the convection becomes turbulent, and irregular. In fact, a solutally convecting solution is likely to develop a changing wave pattern on the interface, which for thick layers may develop into a cellular pattern reminiscent of the effects of constitutional super-cooling in metals (ref 11).

Using the critical Raleigh numbers, it is possible to calculate as in section II.1 and II.2 below the approximate experimental conditions under which stable growth should result.

II.1 Temperature-induced instabilities

The stability criterion

$$\frac{g\gamma}{K\eta} (\Delta x)^4 \left(\frac{\Delta T}{\Delta x} \right) < 1700$$

predicts that solutions of depth Δx will be stable against convection for

$$(\Delta x)^4 \left(\frac{\Delta T}{\Delta x} \right) < 6.45 \quad \text{at } 800^\circ\text{C}$$

Thus stability with respect to thermal gradients will exist for values of Δx less than the values in Table II.1.

TABLE II.1

$\left(\frac{\Delta T}{\Delta x} \right) ^\circ\text{C/cm}$	$\Delta x \text{ cm}$
0.25	2.25
0.5	1.89
1.0	1.59
2.0	1.34
4.0	1.13
5.0	1.07
10.0	0.90

In the present experimental situation where $\left(\frac{\Delta T}{\Delta x} \right) = 4.6^\circ\text{C/cm}$, it is necessary to have $\Delta x < 1.09 \text{ cm}$ to prevent convection developing in the solution.

II.2 Solute-induced instabilities

The stability criterion for solute concentration gradients

$$\frac{g\beta}{D\eta} \left(\frac{\Delta C}{\Delta x} \right) (\Delta x)^4 < 1770$$

is more difficult to analyse than that for temperature gradients. No experimentally determined values exist for β , the change in volume of a solution for unit change in solute concentration.

A complicated formulation by Tiller (ref. 41) may be simplified (ref. 15) for the Ga-As binary system to the form

$$\beta = \frac{M_{As} \left(1 - \frac{\rho_{Ga}}{\rho_{As}} \right)}{C_{Ga}^i M_{Ga} + C_{As}^i M_{As}}$$

where C_{As}^i is the concentration of As at the solid-liquid growth interface.

The density of free As, ρ_{As} , (measured at 20°C) is greater than the density ρ_{Ga} of the solvent, which would tend to discourage solute-induced instabilities. However, there are reasons to believe that As does not exist freely in the solution, but that some chemical bonding Ga-As occurs (ref. 42-44). If the solute As does exist as a Ga-As complex, then we should replace ρ_{As} by ρ_{GaAs} , and M_{As} by M_{GaAs} , in calculating a value for β . Using this assumption, a value for β may be estimated as $2.1 \times 10^{-2}/(g \text{ cm}^{-3})$.

The stability criterion then becomes

$$\left(\frac{\Delta T}{\Delta x} \right) (\Delta x)^4 < \frac{1770 D \eta}{g \beta \left(\frac{\Delta C}{\Delta T} \right)}$$

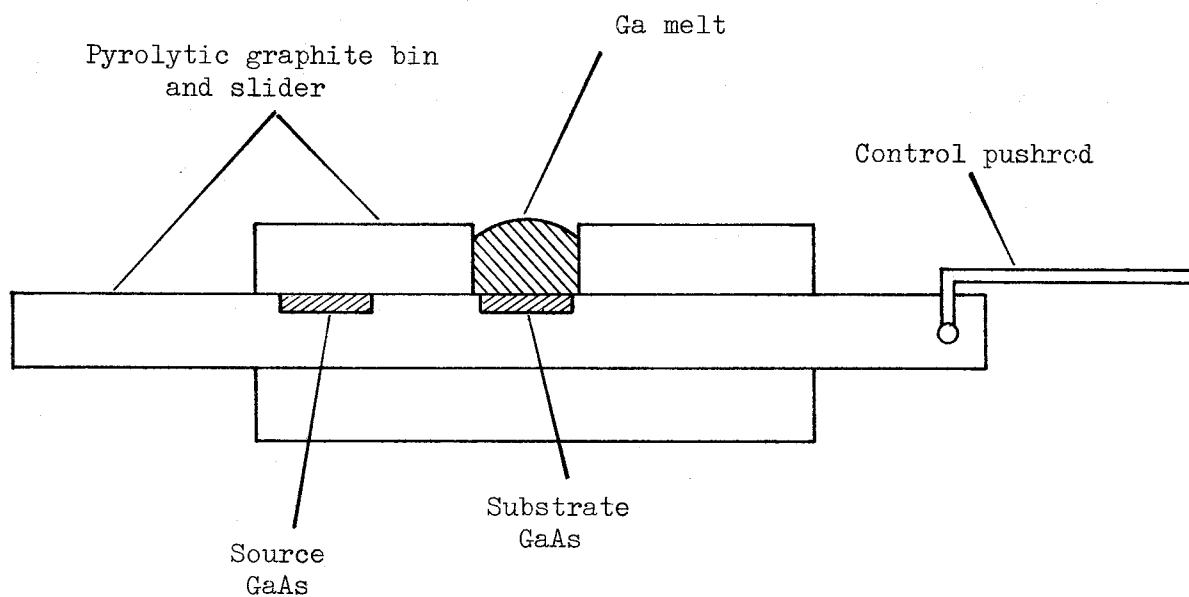
$$\text{i.e.} \quad \left(\frac{\Delta T}{\Delta x} \right) (\Delta x)^4 < 15 \times 10^{-4}$$

This predicts that stability with respect to solute concentration gradients will exist only for values of Δx less than the values in Table II.2.

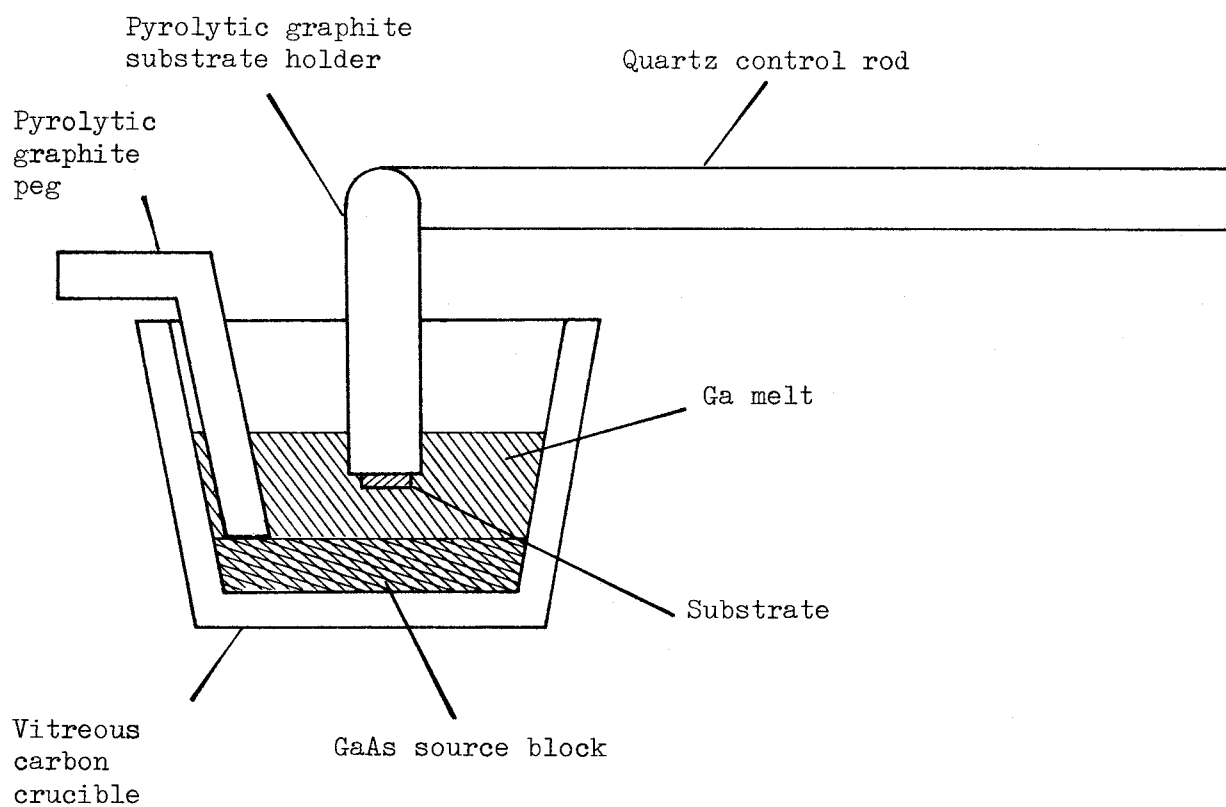
TABLE II.2

$\left(\frac{\Delta T}{\Delta x} \right) \text{ } ^\circ\text{C/cm}$	$\Delta x \text{ cm}$
0.25	2.78×10^{-1}
0.5	2.34×10^{-1}
1.0	1.97×10^{-1}
2.0	1.65×10^{-1}
4.0	1.39×10^{-1}
5.0	1.32×10^{-1}
10.0	1.11×10^{-1}

In the present experimental situation where $\left(\frac{\Delta T}{\Delta x} \right) = 4.6^\circ\text{C/cm}$, it is necessary to have $\Delta x < 0.13 \text{ cm}$ to prevent convection developing.

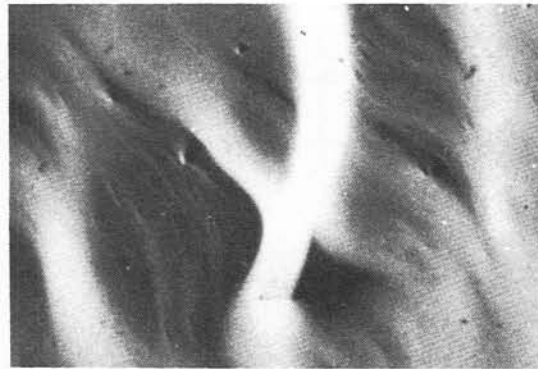
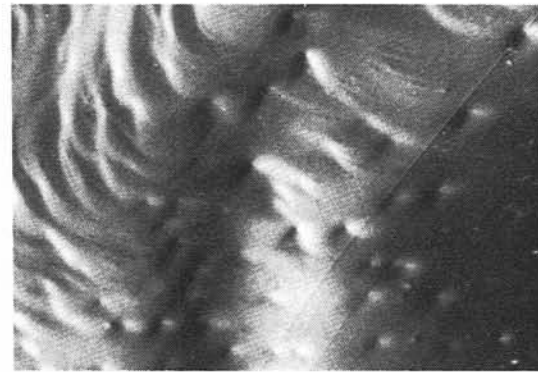
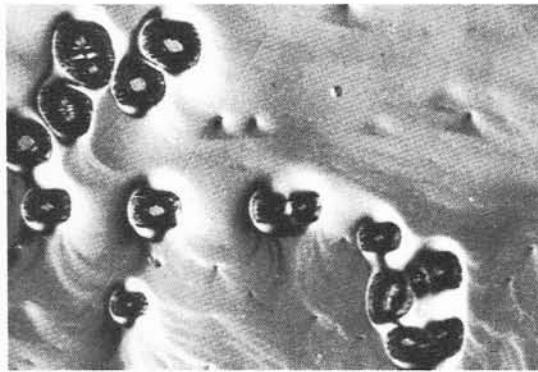
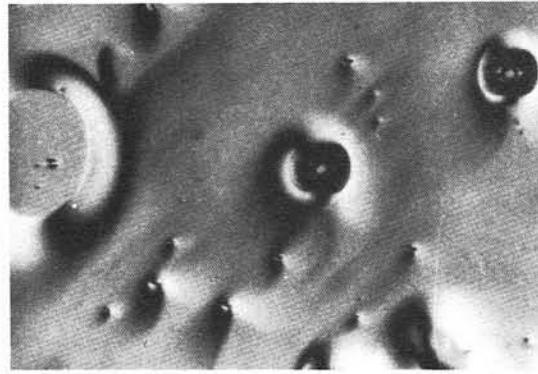
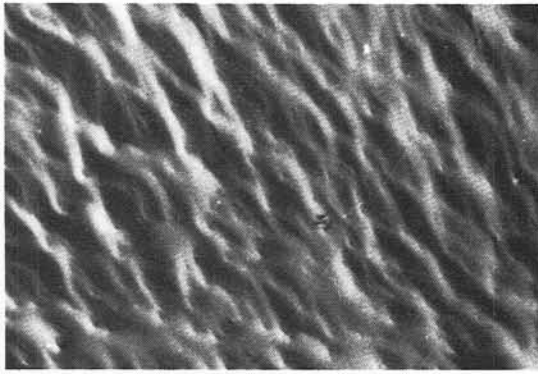


(a) Sliding boat used for the Temperature Transient Technique



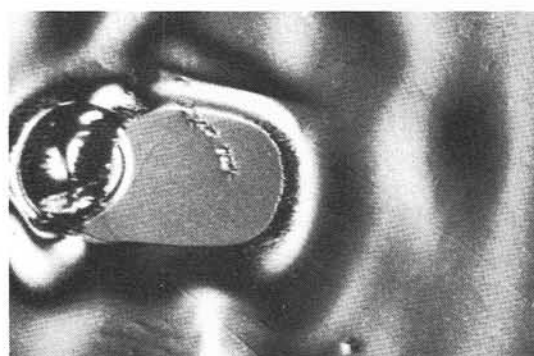
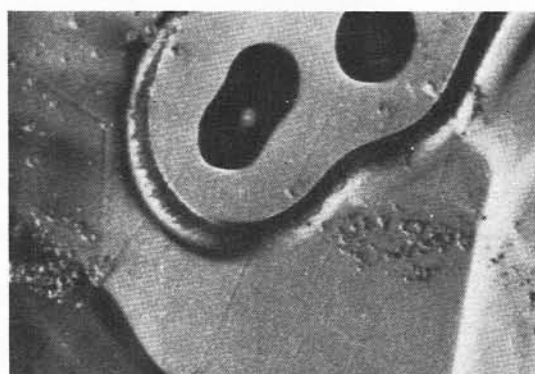
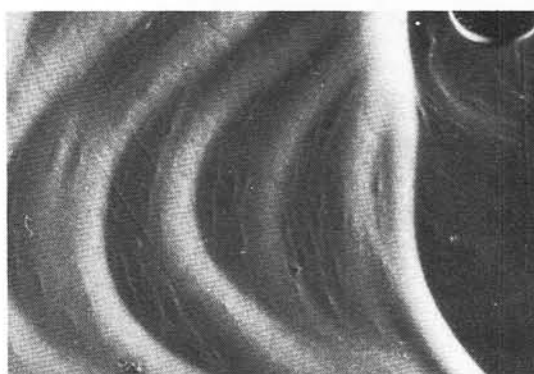
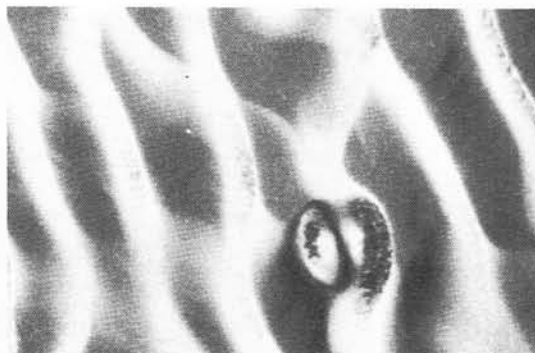
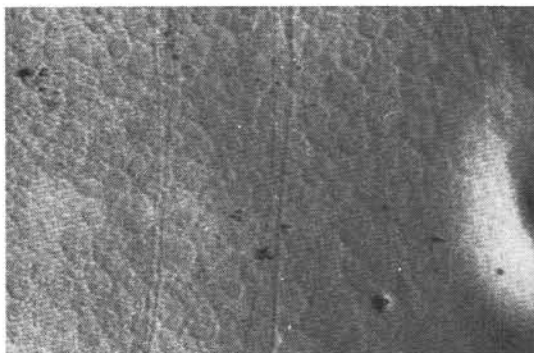
(b) Crucible arrangement used for the Steady State Method

Figure 1. Schematic of apparatus used for liquid phase epitaxial growth of a single layer



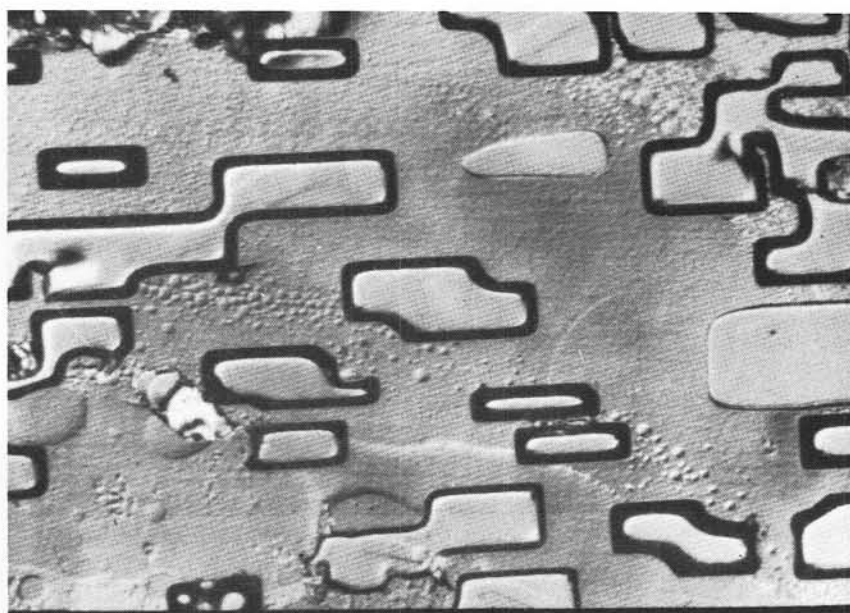
Scale: 71 μ /cm

Figure 2(a). Various surface morphologies observed on Sample 8
(Magnification 140X)



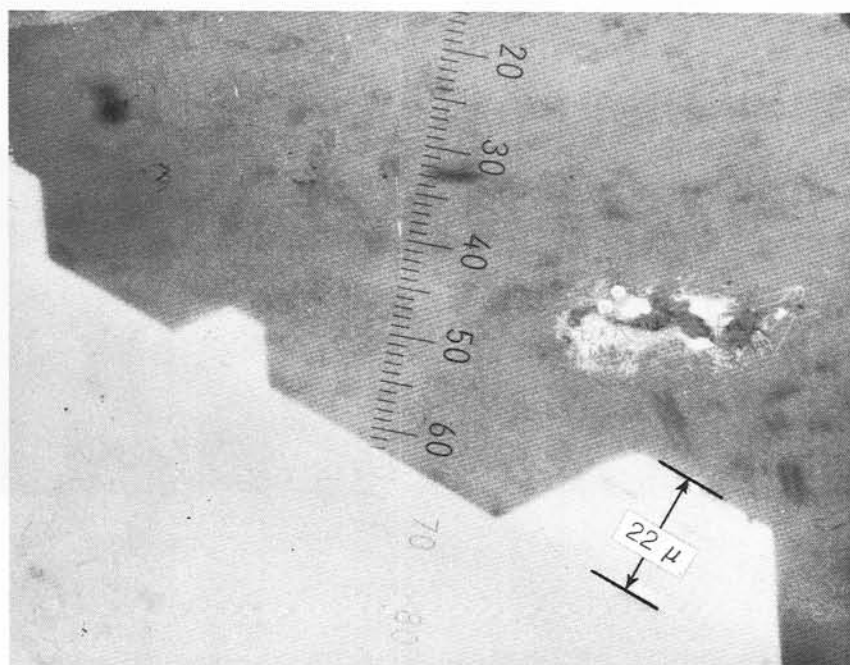
Scale: 71 μ /cm

Figure 2(b). Various surface morphologies observed on Sample 9
(Magnification 140X)



Scale: 28.6 μ /cm

(a) Surface features



Scale: 13.8 μ /cm

(b) Cross-sectional view of cleaved sample

Figure 3. Irregular "mesa" structures formed when the saturated melt does not wet the substrate surface uniformly

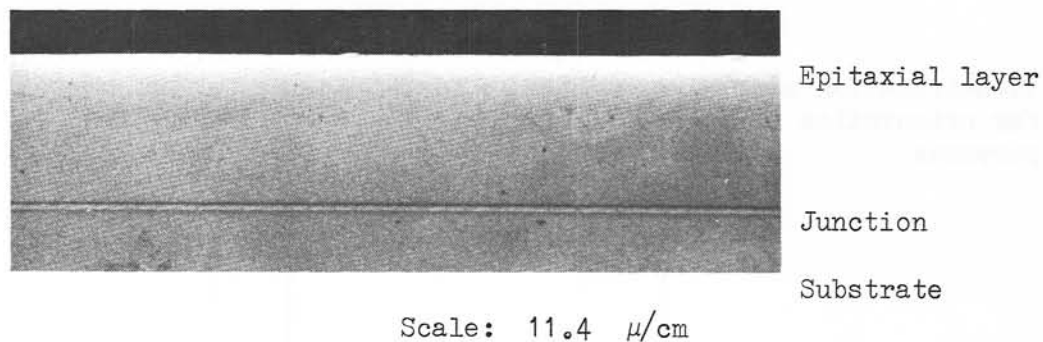


Figure 4. Highly uniform junction formed on a GaAs substrate

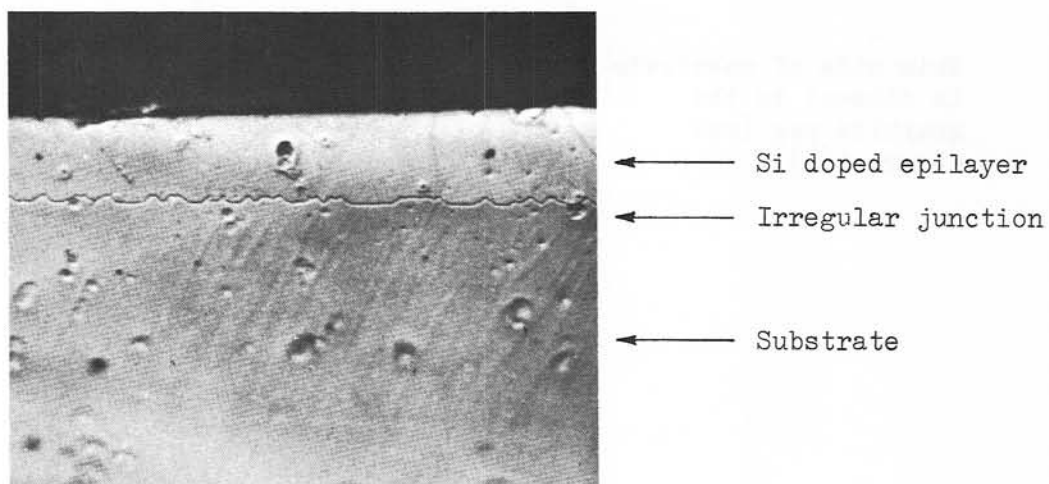


Figure 5. Irregular junction formed after attempts to dope the epitaxial layer with silicon

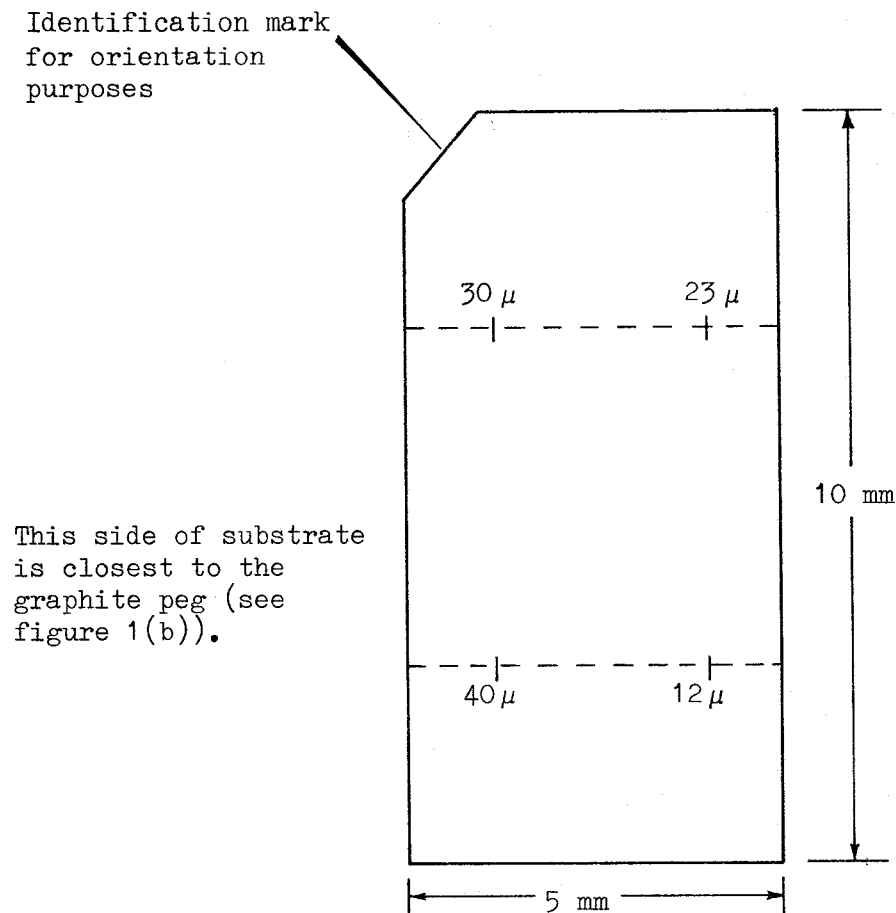


Figure 6. Typical example of the variation in thickness of the epitaxial layers grown using the Steady State Method. The sample shown here was grown over a period of 2 hours, at a nominal temperature of 800°C and with a temperature differential of 50°C applied across the furnace.

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This report discusses two methods of liquid phase epitaxial (LPE) growth applied to the compound semiconductor gallium arsenide, and develops a mathematical description for each using a diffusion-limited model.

The properties of the epitaxial layers grown under various experimental conditions are discussed, and the observed growth rates compared with those predicted by the mathematical models. From the differences observed, it is concluded that processes additional to simple diffusion of solute through the melt are occurring. Convective mixing caused by horizontal temperature gradients within the melt is suggested as an explanation for these differences.